Aperiodic Crystals: How is that even possible?

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Liquid to Crystal Phase Transition

(Landau) Theory of Symmetry Breaking:

- What is the order parameter?
- What is the broken symmetry?
  - What is the nature of the order-parameter space?
- What are the elementary excitations?
- What are the topological defects?

R. Lifshitz, Symmetry breaking in the age of quasicrystals, Isr. J. Chem. 51 (2011) 1156.

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But first, what is a crystal?

R. Lifshitz, Symmetry breaking in the age of quasicrystals, Isr. J. Chem. 51 (2011) 1156.

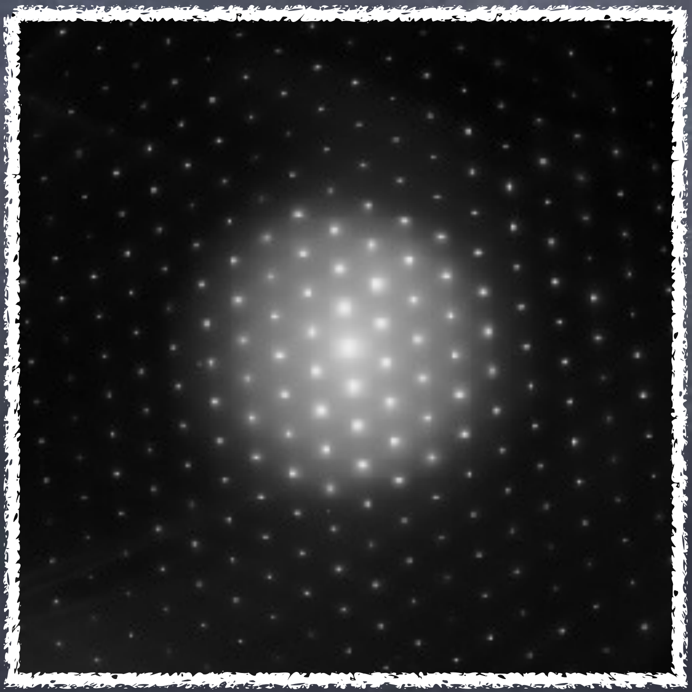
What is a crystal?

- Before Shechtman (1982):

  An ordered solid, and therefore periodic.

  - Diffraction (Fourier transform) contains Bragg peaks, whose positions are closed under vector addition, forming a discrete periodic lattice (only 14 Bravais classes in 3d).
  - Restricted rotation symmetries (n=2,3,4,6).

Purple Quartz Amethyst crystal.



R. Lifshitz, "What is a crystal?", Z. Kristallogr. 222 (2007) 313.

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- After Shechtman (1982):

  An ordered solid, not necessarily periodic.

  - Diffraction (Fourier transform) contains Bragg peaks, whose positions are closed under vector addition, but arbitrary.
  - Unrestricted rotation symmetry.

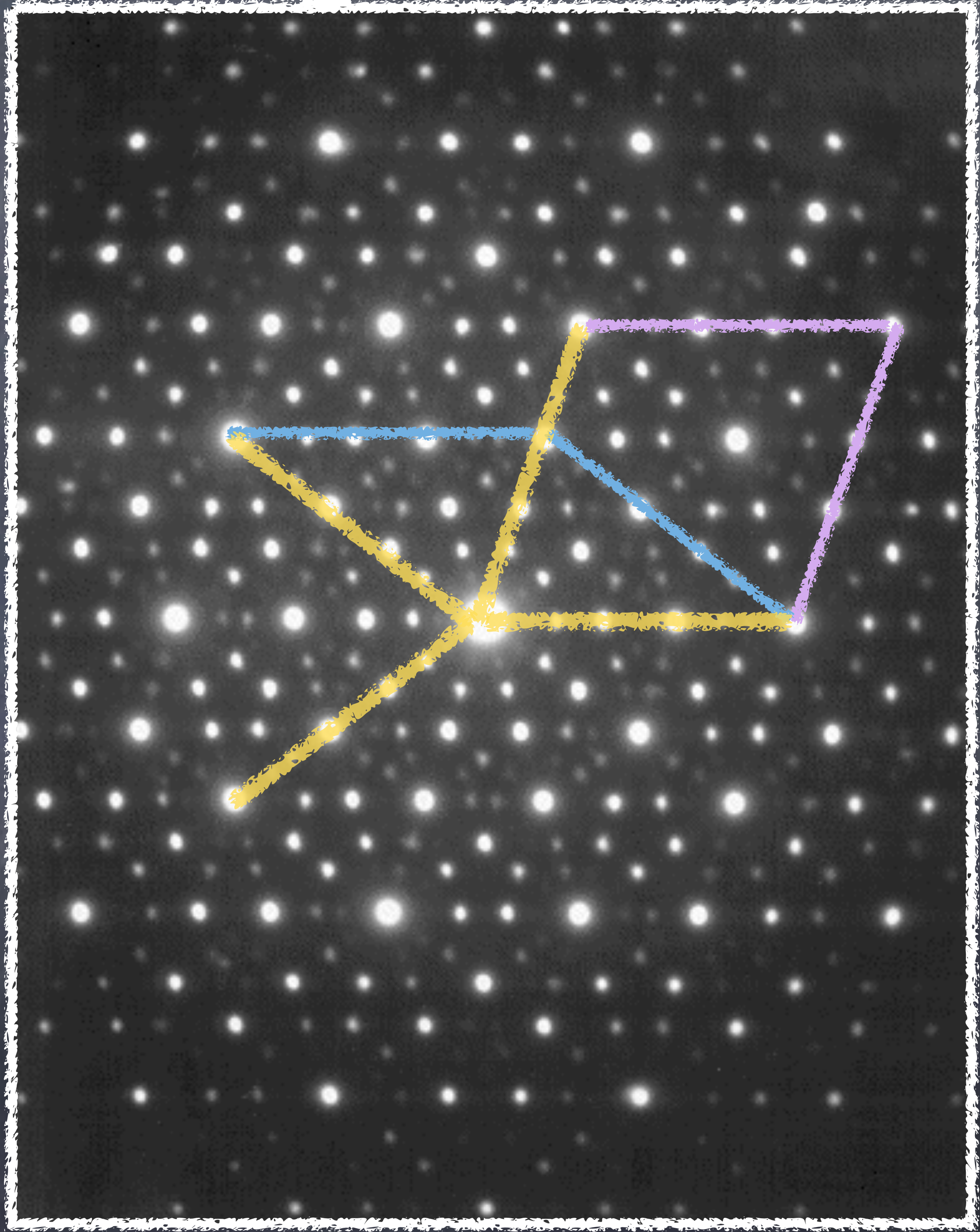
R. Lifshitz, “What is a crystal?”, Z. Kristallogr. 222 (2007) 313.

What is a Crystal?

A crystal is a solid with long-range order; one whose diffraction diagram contains Bragg peaks.

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}\in\mathbf{L}} \rho(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

r = rank, d = dimension	
r=d	Periodic
d≤r<∞	Quasiperiodic
d≤r≤∞	Almost periodic



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R. Lifshitz, "What is a crystal?", Z. Kristallogr. 222 (2007) 313.

What is the order parameter?

- Order Parameter:

  $\rho(\mathbf{r})$ = density - average density

  - Above T_c zero everywhere
  - Below T_c nonzero with Bragg Peaks in $\rho(\mathbf{k})$
- Free Energy: A functional of $\rho(\mathbf{r})$ that preserves the symmetries of the liquid state
  - F is zero if $\rho(\mathbf{r}) = 0$ everywhere
  - In liquid state F is positive for nonzero $\rho(\mathbf{r})$
  - In crystal state F is negative for nonzero $\rho(\mathbf{r})$

N.D. Mermin, Phys. Rev. 176 (1968) 250-254.

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What is the broken symmetry?

- Consider a spontaneous breaking of the symmetry to a quasiperiodic crystal,

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}\in\mathbf{L}} \rho(\mathbf{k}) \mathbf{e}^{\mathbf{ik}\cdot\mathbf{r}}$$

Periodic crystal if r = d, quasicrystal if r > d.

- In Fourier space the free energy expansion is

$$\mathcal{F} = \sum_n \sum_{\mathbf{k}_1\ldots\mathbf{k}_n\in L} A(\mathbf{k}_1\ldots\mathbf{k}_n)\,\rho(\mathbf{k}_1)\ldots\rho(\mathbf{k}_n)$$

where the coefficients $A(\mathbf{k}_1\ldots\mathbf{k}_n)$ must vanish unless $\mathbf{k}_1 + \ldots + \mathbf{k}_n = 0$ (Exercise: why is that?).

What is the relation between different minima of F?

What is the broken symmetry?

What is the relation between different minima of F?

$$\mathcal{F} = \sum_n \sum_{\mathbf{k}_1 \ldots \mathbf{k}_n \in L} A\left(\mathbf{k}_1 \ldots \mathbf{k}_n\right) \rho\left(\mathbf{k}_1\right) \ldots \rho\left(\mathbf{k}_n\right)$$

- Two densities $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ are both minimum free-energy states only if their Fourier amplitudes satisfy

  Structure Invariants

  $$\forall \mathbf{k}_1 \ldots \mathbf{k}_n \in L : \rho'\left(\mathbf{k}_1\right) \ldots \rho'\left(\mathbf{k}_n\right) = \rho\left(\mathbf{k}_1\right) \ldots \rho\left(\mathbf{k}_n\right)$$

  for any n, whenever $\mathbf{k}_1 + \ldots + \mathbf{k}_n = 0$.

- In real space: Identity of the nth order autocorrelation functions

  $$C^{(n)}\left(\mathbf{r}_1, \ldots, \mathbf{r}_n\right) = \lim_{V \to \infty} \frac{1}{V} \int_V \mathrm{d}\mathbf{r} \rho(\mathbf{r}_1 - \mathbf{r}) \cdots \rho(\mathbf{r}_n - \mathbf{r})$$

What is the broken symmetry?

What is the relation between different minima of F?

Two different minimum free-energy states, sharing the same n-point autocorrelation functions for arbitrary n, are indistinguishable.

- 2-point correlation (Patterson Function): The two densities have identical diffraction diagrams. Their Fourier amplitudes differ at most by a phase: $\forall \mathbf{k} \in L: \quad \rho'(\mathbf{k}) = e^{2\pi i \chi(\mathbf{k})} \rho(\mathbf{k})$.
- 3-point correlation: $\chi(\mathbf{k})$, called a gauge function, is a linear function of the wave vectors in L

$$\forall \mathbf{k}_1, \mathbf{k}_2 \in L: \chi(\mathbf{k}_1 + \mathbf{k}_2) = \chi(\mathbf{k}_1) + \chi(\mathbf{k}_2)$$

N.D. Mermin, Rev. Mod. Phys. 64 (1992) 3-49.

What is the broken symmetry?

What is the relation between different minima of F?

All the different minima of F are related by gauge functions - the set of all gauge functions can be used to label all the minima and characterize the order parameter space!!

- Because gauge functions are linear, once we choose a basis $\mathrm{b}^{(i)}$(with i =1...r) for L, each gauge function is uniquely expressed by r real numbers

$$\chi_i = \chi\left(\mathbf{b}^{(i)}\right) \text{ with } i = 1 \ldots r.$$

The set of all gauge functions is an r-dimensional vector space V* over the real numbers.

Rigid translations and phasons

What is the relation between different minima of F?

- The effect of any gauge function can be decomposed into a pure d-dimensional rigid translation, given by the d components of a translation vector $\mathbf{u}$ and a remaining contribution $\varphi(\mathbf{k})$, called a phason.
- This is achieved by a change of basis in V*

$$\chi(\mathbf{k}) = \sum n_i \chi_i = \frac{\mathbf{u}\cdot\mathbf{k}}{2\pi} + \varphi(\mathbf{k}), \text{ where } \mathbf{k} = \sum n_i \mathbf{b}^{(i)}.$$

  - For periodic crystals $\varphi(\mathbf{k}) = 0$, and $\mathbf{u} = \sum \chi_j \mathbf{a}^{(j)}$, where $\mathbf{a}^{(j)} \cdot \mathbf{b}^{(i)} = 2\pi\delta_{ij}$.
  - For quasicrystals $\varphi(\mathbf{k})$ has r-d degrees of freedom.

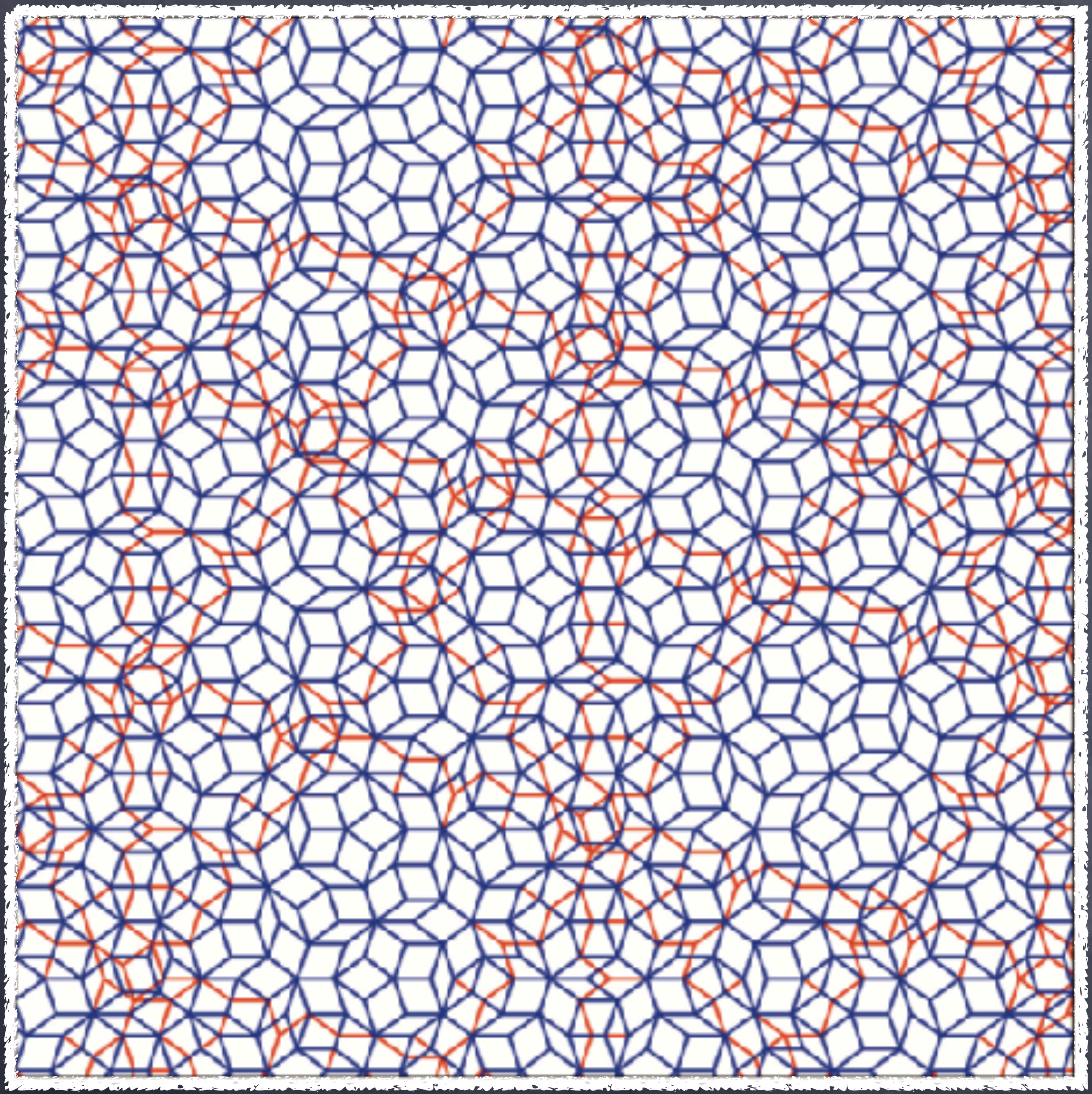
What remains of the broken symmetry?

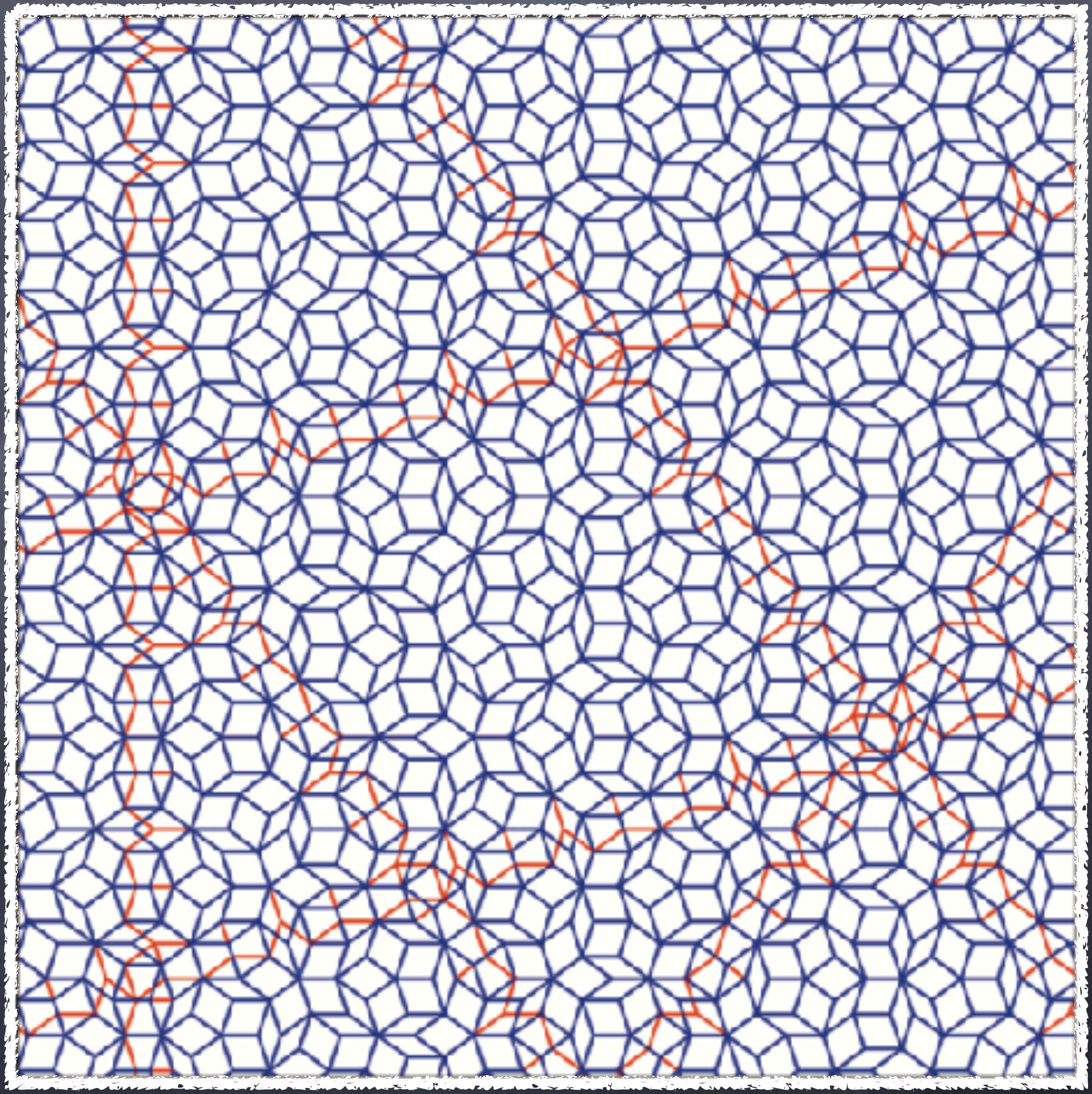
What are the gauge functions that leave the broken-symmetry state invariant rather than taking it into other minimum free-energy states?

$$\forall \mathbf{k} \in L : \quad \rho'(\mathbf{k}) = e^{2\pi i \chi(\mathbf{k})} \rho(\mathbf{k})$$

L* = the set of integer-valued gauge functions!!

Rigid Translation of the Penrose tiling





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What are the gauge functions that take a given minimum free-energy state into all other minima?

V*/L* = the gauge functions in V* modulo L*

Every degenerate ordered state is parameterized by a set of r numbers $0 \leq \chi_i < 1, i = 1...r$.

The order-parameter space is an r-dim. torus!!

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Goldstone modes - phonons & phasons

Long wavelength deformations of an ordered state that cost very little energy.

- Any gauge function $\chi(\mathbf{k})$ transforms one ordered state into another at no energy cost.
- Slightly change the gauge function as you move along the crystal at a small energy cost,

$$(\chi_1, \ldots, \chi_r) \longrightarrow \chi_i(\mathbf{r}) \sim e^{i\mathbf{q}\cdot\mathbf{r}}$$

This is an r-component deformation field!

- Often described in the phonon-phason basis.

$$\chi(\mathbf{r};\mathbf{k}) = \sum n_i \chi_i(\mathbf{r}) = \frac{1}{2\pi}\mathbf{u}(\mathbf{r})\cdot\mathbf{k} + \frac{1}{2\pi}\mathbf{w}(\mathbf{r})\cdot\tilde{\mathbf{k}}$$

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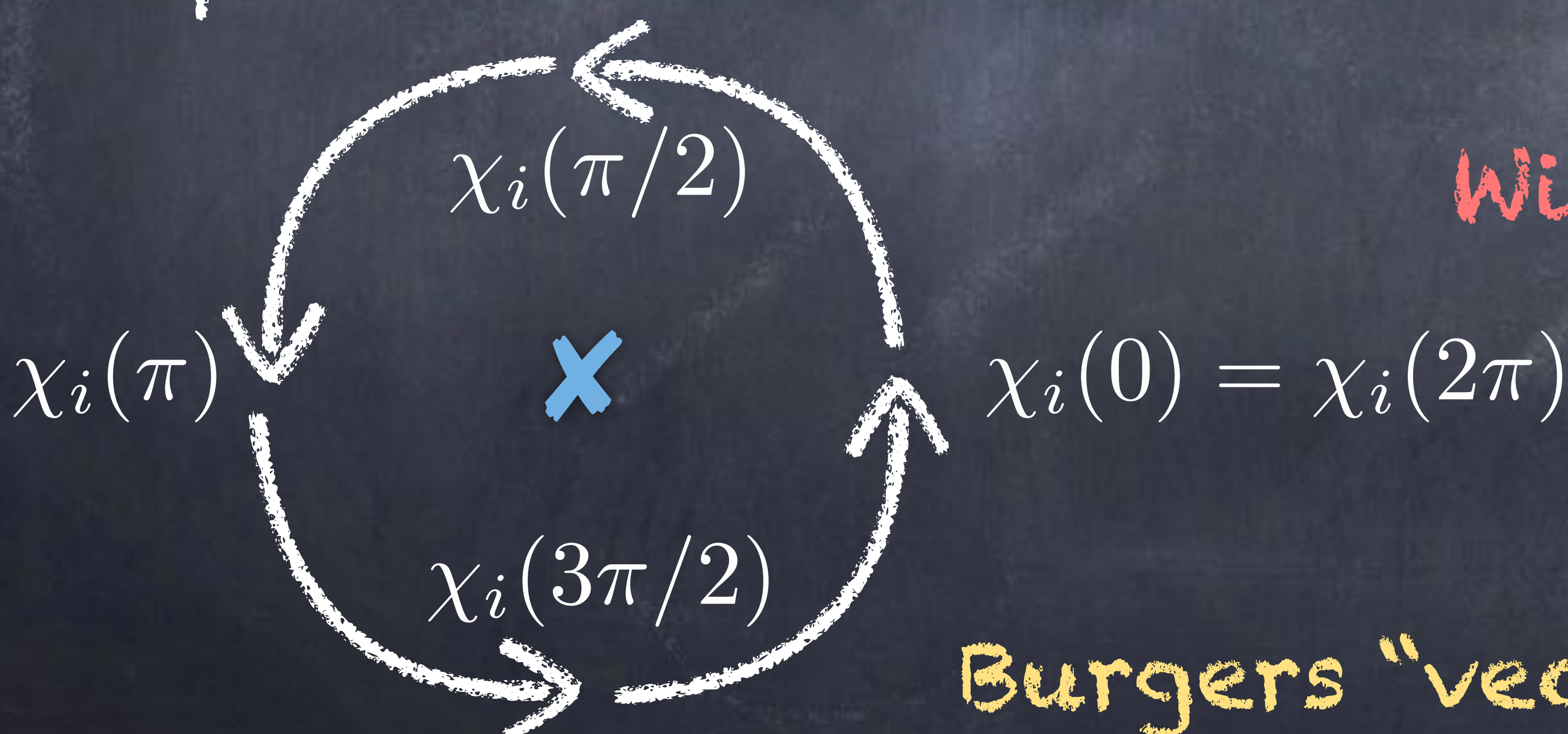
Dislocations

Away from the core of the dislocation the crystal is in one of its ordered states (only-slightly strained).

- Again, use the r-component field $\chi_i(\mathbf{r})$, but now go in a loop around the core position, until you return to the starting point.
- In polar coordinates (in 2d): $\chi_i(r,\theta) \longrightarrow \chi_i(\theta)$.

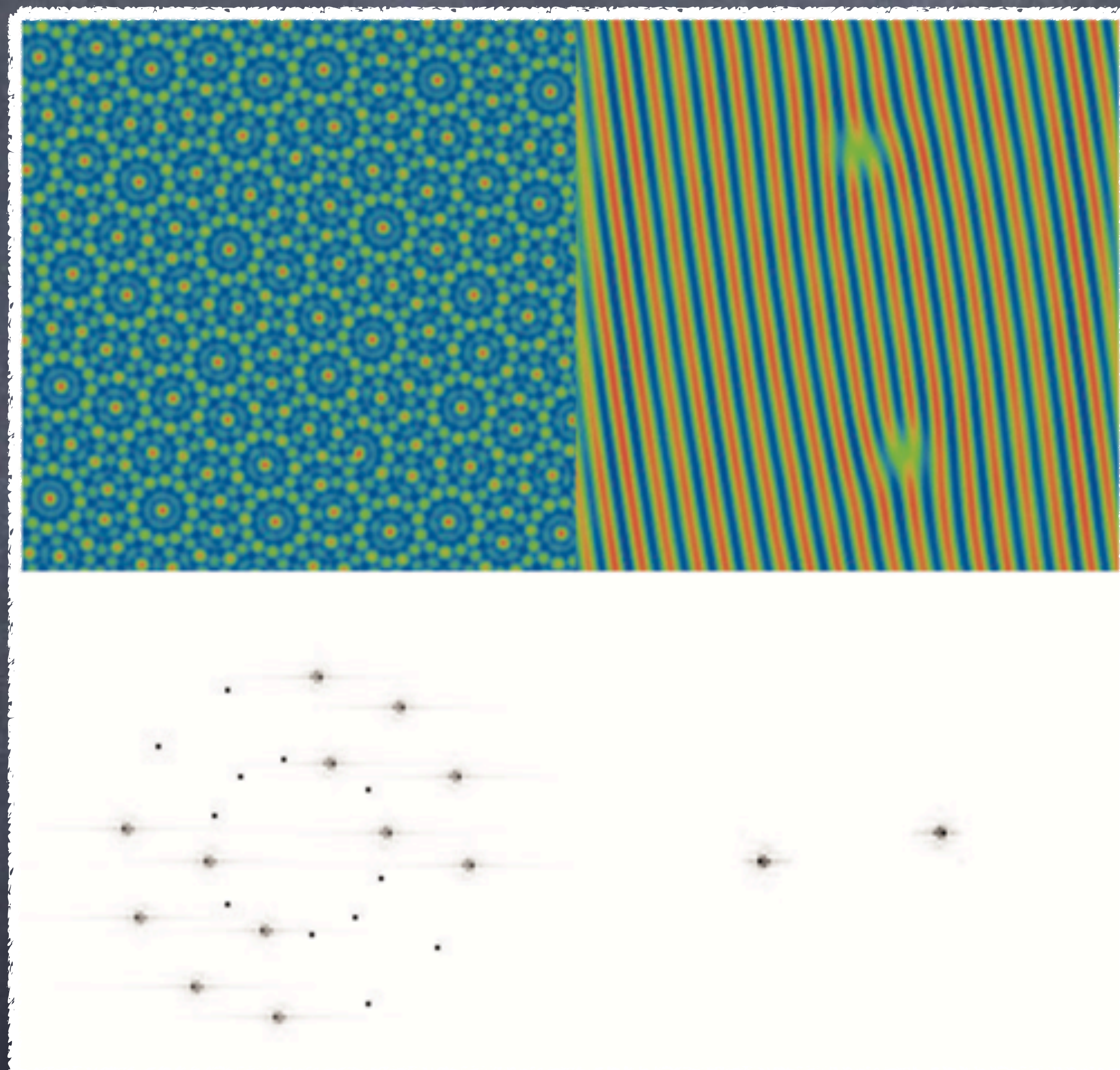


Winding numbers

$$\chi_i(\theta) = n_i\theta$$

Burgers "vector": $(n_1, \ldots, n_r)$

Seeing Dislocations



Fourier space

Filtering of Bragg peaks

Back to real space, where now the dislocations are obvious

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The gauge function: $$\rho'(\mathbf{k}) = e^{2\pi i\chi(\mathbf{k})}\rho(\mathbf{k})$$

R. Lifshitz, Symmetry breaking in the age of quasicrystals, Isr. J. Chem. 51 (2011) 1156.

Further reading

- Main reference for this lecture:
  - R. Lifshitz, "Symmetry breaking in the age of quasicrystals", Isr. J. Chem. 51 (2011) 1156.
- Basic terminology and definitions:
  - R. Lifshitz, "What is a crystal?", Z. Kristallogr. 222 (2007) 313.
  - R. Lifshitz, "Quasicrystals: A matter of definition", Found. Phys. 33 (2003) 1703.
- Symmetry of crystals:
  - N.D. Mermin, "The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic, and triclinic crystals", Rev. Mod. Phys. 64 (1992) 3.
  - R. Lifshitz, "The Symmetry of Quasiperiodic Crystals", Physica A 232 (1996) 633.
  - R. Lifshitz, "Theory of color symmetry for periodic and quasiperiodic crystals", Rev. Mod. Phys. 69 (1997) 1181.

Further reading

- Symmetry of crystals (cont.):
  - R. Lifshitz, "Magnetic point groups and space groups", Encyclopedia of Condensed Matter Physics, Vol. 3, Ed. F. Bassani, G.L. Liedl, and P. Wyder, (Elsevier Science, Oxford, 2005) 219.
- Phonons & Phasons:
  - B. Freedman, R. Lifshitz, J.W. Fleischer, and M. Segev, "Phason dynamics in nonlinear photonic quasicrystals", Nature Materials 6 (2007) 776.
- Dislocations:
  - G. Barak and R. Lifshitz, "Dislocation dynamics in a dodecagonal quasiperiodic structure", Phil. Mag. 86 (2006) 1059.
  - L. Korkidi, K. Barkan, and R. Lifshitz, "Analysis of dislocations in quasicrystals composed of self-assembled nanoparticles", In Aperiodic Crystals, (Springer, Dordrecht, 2013) ch. 16.

Most articles are available at: http://www.tau.ac.il/~ronlif/pub.html